

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF APPEALS AND INTERFERENCES

In re application of)	
)	
JOLINDE MACHTELD VAN DE GRAAF and)	
THIJME LAST)	
)	
Serial No. 10/533,172)	Group Art Unit: 1797
)	
Filed April 29, 2005)	Examiner: Frank M. Lawrence Jr.
)	
REMOVAL OF SULPHUR COMPOUNDS FROM)	March 21 2008
HYDROCARBON STREAMS USING)	
ADSORBENTS AND REGENERATION)	
OF THE LOADED ADSORBENTS)	
)	

COMMISSIONER FOR PATENTS
P. O. Box 1450
Alexandria, VA 22313-1450

Sir:

APPEAL BRIEF

This brief is filed in support of Applicant's appeal from the Examiner's action mailed October 26, 2007, finally rejecting claims 1, 5-8, 10-12, 14, 16, 18-21 and 23-25 in the above-identified U.S. patent application. A notice of appeal from this decision was filed by Applicant on January 24, 2008.

Please charge the fee for filing this brief to Shell Oil Company Deposit Account No. 19-1800.

It is respectfully requested that the Board reverse the final rejection of claims 1, 5-8, 10-12, 14, 16, 18-21 and 23-25 of the above-identified application for the reasons discussed below.

Real party in interest

The invention described and claimed in the above-identified patent application is assigned to Shell Oil Company, which is the real party in interest in the present appeal.

Related appeals and interferences

Appellant and Appellant's legal representatives are not aware of any related appeals or interferences.

Status of claims

Claims 1, 5-8, 10-12, 14, 16, 18-21 and 23-25 have been rejected and are the subject of this appeal.

A copy of all of the claims on appeal can be found in the Claims Appendix.

Status of amendments

The amendment filed subsequent to the final rejection was entered according to the advisory action mailed February 11, 2008.

Summary of claimed subject matter

The subject matter claimed is process for removing sulfur compounds and water from a hydrocarbon stream, such as natural gas, which includes a first step of removing water from the hydrocarbon stream using a zeolite having a pore diameter of less than 5 Å, and thereafter contacting the hydrocarbon stream with a zeolite having a pore diameter of at least 5 Å to adsorb sulfur compounds thereon to provide a sulfur loaded adsorbent, followed by regeneration of the sulfur loaded adsorbent with a regeneration gas stream having a specified relative humidity, e.g. less than 100 %, preferably 30 % or less, e.g., 10-30 %. (Specification, page 5, lines 19-22, page 6, lines 21-29, page 9, lines 15-23, page 11, lines 22-32). The inventive process utilizing a regeneration gas having the specified relative water humidity, significantly reduces the degradation/ageing of sulfur loaded zeolite adsorbents and reduces coke formation extending their economic life (Specification, page 3, lines 25-32).

Grounds of rejection to be reviewed on appeal

The rejection of claims 1, 5-7, 14, 16, 18 and 19 under 35 U.S.C. §103(a) as being unpatentable over the U.K. Patent Application (GB 2275625 A) in view of Gingrich et al (U.S. 6,074,459).

The rejection of claims 1, 7, 8 10-12, 14, 16, 20, 21 and 23-25 under 35 U.S.C. §103(a) as being unpatentable over Sherman et al (US 4,329,160) in view of Gingrich et al (U.S. 6,074,459) and taken together with Turnock et al (US 3,620,969).

Argument

The Rejection of Claims 1, 5-7, 14, 16, 18 and 19 under 35 U.S.C. §103(a) as Being Unpatentable over the U.K. Patent Application (GB 2275625 A) in View of Gingrich et al (U.S. 6,074,459) is Erroneous and Should be Reversed.

The present invention is based in part on the discovery that the degradation/ageing of sulfur loaded zeolite adsorbents used to remove sulfur from gaseous hydrocarbon streams can be significantly reduced by regenerating the adsorbents using a regeneration gas having a specified small amount of water present in the regenerating gas (Specification, page 3, 25-32). The presence of small amount of water in the regenerating gas, i.e., “wet” regeneration, has been found to extend the capacity of the adsorbent through repeated adsorption/regeneration cycles. This is shown in Table 1 on page 13 of the present application, where the capacity of the adsorbent after 50 cycles of conventional “dry” regeneration was reduced from 19.2 to 12.1 (a 37% decrease) while the capacity of the adsorbent after 50 cycles of “wet” regeneration in accordance with the invention was reduced from 17.4 to 16.7 (only a 4 % decrease). This is rather surprising in that presence of water under certain conditions has been known to cause hydrothermal ageing of zeolite adsorbents, reducing the economic life of a zeolite adsorbent, rather than extending it as is the case with the present process.

Each of the claims rejected over a combination of GB ‘625 and Gingrich et al, either directly or through dependency, contains a limitation requiring that the regeneration gas used to regenerate the sulfur loaded adsorbent contain a certain amount of water expressed in terms of relative humidity. I.e., claims 1, 5, 6, 14, 16, 18, and 19 specify the regeneration gas have a relative humidity of 30 % or less, while claim, 7 specifies a relative humidity less than 100%.

GB 2,275,625 (GB'625)

Turning now to the prior art, GB '625 patent teaches a process for removing hydrogen sulfide and organic sulfur from a gas stream by first passing it to an absorber system wherein it is contacted with an aqueous absorbent to remove hydrogen sulfide and mercaptans therefrom. The thus-treated gas having a decreased content of hydrogen sulfide and mercaptans is then passed to an adsorbent system such as first adsorber 22, in Fig. 1/1, wherein it is contacted with a solid adsorbent such as a molecular sieve to remove additional mercaptans and water therefrom to provide a purified gas stream. The solid adsorbent is thereafter regenerated in a second adsorber 23 using a bleed stream of the purified gas which flows through heater 44 and conduit 31b. Since any water present in the feed gas to first adsorber 22 will be removed by the by the adsorbent in first adsorber 22, the regeneration of the adsorbent in second adsorber 23 with a bleed stream of purified gas in the second adsorber 23 is a conventional "dry" regeneration. There simply is no teaching or suggestion in GB '625 of "wet" regeneration using a regeneration gas stream having a specified relative humidity to regenerate the loaded adsorbent.

One of the disclosures in GB '625 cited on page three of the final Office action, is actually believed to support Appellant's position rather than the Examiner's. The disclosure on page 4, lines 12-18 of GB '625, cited in the final Office action reads:

"The solid adsorbent can in addition to removing mercaptans remove water from the treated gas. With the regeneration off-gas water is removed from the solid adsorbent, and to remove water from the regeneration off-gas the regeneration off-gas is cooled in a cooler (not shown) and liquid water is separated in a gas-liquid separator (not shown) which cooler and separator are arranged in conduit 47".

These statements support the fact that the regeneration of the adsorbent in GB '625 is a "dry" regeneration process, since it is disclosed the solid adsorbent, such as the adsorbent used in the first adsorber 22, will remove water in addition to removing mercaptans from the treated gas. Hence, the "bleed stream of purified gas" used for regeneration of adsorbent in second adsorber 23 would be expected to contain essentially no water, since any water in the feed gas to first adsorber 22 would be removed by the adsorbent in adsorber 22, together with the sulfur compounds. Thus, any water that appears in the regeneration off-gas, is water that was removed from the adsorbent during regeneration. It is not water that was present in, or added to, the bleed stream of purified gas to produce a relative humidity. There is absolutely no indication that the bleed stream of purified gas used for regeneration in GB '625 contains a relative water humidity,

nor is there any teaching or suggestion in GB '625 that regeneration with a regeneration gas containing a specified relative humidity will significantly reduce degradation/ageing of a zeolite adsorbent or prevent coke formation, as discovered by Applicant.

Gingrich et al

Gingrich et al teaches a process for removing contaminants from a gas stream to unprecedentedly low levels by the use of four sequential beds of solid adsorbents. The first bed of adsorbent is used to remove water, while the following beds are used to remove various types of sulfur compounds and other contaminants such as fluorocarbons and halocarbons. Gingrich et al does not contain any teaching or suggestion relating to regeneration of any of any of the adsorbents used in any of the four sequential beds. The concept of a regeneration gas stream having a specified relative humidity is totally lacking in Gingrich et al, which apparently is only being cited for its teaching of a first adsorbent bed to remove water prior to a second and third adsorbent bed to remove sulfur-containing compounds.

Thus, it can be seen that neither GB '625 nor Gingrich et al teach or suggest regenerating a sulfur loaded adsorbent by contacting the loaded adsorbent with a regeneration gas stream having a specified relative humidity. Since claims 1, 5-7, 14, 16, 18 and 19, each contain a limitation as to the relative humidity of the regenerating gas stream, which contributes to the significantly reduced degradation/ageing of the regenerated adsorbent, all of these claims are believed to be patentable over this combination of references. Accordingly, the rejection of these claims on the basis of GB '625 and Gingrich et al is erroneous and should be reversed.

The Rejection of Claims 1, 7, 8, 10-12, 14, 16, 20, 21 and 23-25 under 35 U.S.C. §103(a) as Being Unpatentable over the Sherman et al (US 4,329,160) in View of Gingrich et al (U.S. 6,074,459) and Taken Together with Turnock et al (US 3,620,969) is Erroneous and Should be Reversed.

In addition to the regeneration of the sulfur loaded adsorbent with a regeneration gas stream having a specified relative humidity to significantly to reduce the degradation/ageing of the adsorbent, another important feature of the present invention is that water is removed from the hydrocarbon feed stream with an adsorbent comprising a first zeolite having a pore diameter of less than 5Å, prior to contacting the hydrocarbon stream with a second zeolite adsorbent having a pore diameter of at least 5Å to adsorb the sulfur compounds. Appellant respectfully submits that process recited in claims 1, 7, 8, 10-12, 14, 16, 20, 21, and 23-25, each of which

claims contain limitations as to these important features, are patentable over Sherman et al, Gingrich et al or Turnock et al, either alone or in combination, as discussed below.

Sherman et al

Sherman et al teaches a process for purifying hydrocarbon gas streams containing H₂S and CO₂ as impurities using molecular sieve adsorbents, wherein the principle object of the invention is to provide a means to suppress the formation of COS (Col. 1, lines 59-63). The basic process disclosed in Sherman et al includes the steps of (a) an adsorption purification stroke wherein H₂S is selectively removed and a substantially H₂S-free hydrocarbon product is recovered; (b) a purge desorption stroke wherein a portion of the hydrocarbon product is heated and passed countercurrently through the adsorption bed to desorb substantially all of the adsorbate molecules selectively adsorbed in step (a); and (c) a cool down stroke wherein the bed is cooled down by cocurrent purge using a portion of the H₂S-free hydrocarbon product. The improvement claimed in Sherman et al is the use of a particular zeolite having a pore diameter of at least 5 Å and at least 45 % of the framework of aluminum atoms being associated with at least one species of an alkaline earth metal cation having an atomic number of less than 56, and injecting into the hydrocarbon stream prior to step (b) a sufficient amount of water vapor to import a substantially uniform adsorbed water loading of from 0.7 to 3.0 wt % to the molecular sieve adsorbent (Col. 2, lines 14-25).

There is no teaching or suggestion in Sherman et al of removing water from hydrocarbon gas stream using a zeolite having a pore diameter less than 5 Å prior to contacting it with the molecular sieve having a pore diameter of at least 5 Å to remove sulfur compounds.

While Sherman et al does teach the injection of water vapor into the hydrocarbon stream prior to purge step (b), the purpose of the addition of water vapor is to import a substantially uniform adsorbed water loading of 0.7 to 3.0 wt % to the molecular sieve adsorbent, which percentage of water has been found to suppress COS formation. There is no teaching or suggestion in Sherman et al that using a regeneration gas having the amounts of relative water humidity specified in Appellant's claims will substantially reduce the degradation/ageing of the adsorbent as discovered by Applicant.

A teaching of the injection of water to achieve a certain water loading a molecular sieve in order to suppress COS formation, would not make obvious to one skilled in the art to use a regeneration gas having a specific relative humidity to substantially reduce the degradation/ageing of the adsorbent being regenerated.

Gingrich et al

As discussed above, Gingrich et al teaches a process for removing contaminants from a gas stream to very low levels by the use of four sequential beds of solid adsorbents. The first bed of adsorbent is used to remove water, while the following beds are used to remove various types of sulfur compounds and other contaminants such as fluorocarbons and halocarbons. Gingrich et al does not contain any teaching or suggestion relating to regeneration of any of any of the adsorbents used in any the four sequential beds.

Turnock et al

Turnock et al discloses a process for removing sulfur compounds from liquid hydrocarbon streams, such as natural gasoline, using a zeolitic molecular sieve dehydrated only to the extent that it contains a residual loading of water of from about 2 to about 5 weight percent (Col.1, lines 4-10).

It is stated in column 2, lines 4-14 of Turnock et al that:

“In accordance with the present invention it has been surprisingly found that the presence of relatively large amounts of residual adsorbed water on large pore zeolitic molecular sieve adsorbents does not diminish their capacity for adsorbing sulfur-containing impurities from liquid hydrocarbon streams. In marked contrast to this finding, it is well known that in vapor phase-sweetening processes, the presence of even relatively small amounts of water on the molecular sieve adsorbent has such an adverse effect on its selectivity and capacity as to render the operation commercially unfeasible”.

According to Turnock et al the above-described discovery makes it possible to carry out the thermal-swing desorption of the sulfur-containing compounds from the molecular sieve adsorbent using a purge gas having a high water content. It is even possible, and in fact preferred, to use steam as the purge gas (col. 2, lines 29-36). The water contents needed in the regeneration gas at various temperatures and pressures to leave from about 2 wt. % to about 5 wt. % H₂O on the adsorbent are given in col. 6, lines 5-31.

Thus, in its most relevant aspects, Turnock et al discloses a thermal-swing desorption step using a purge gas having a high water content, preferably steam, to regenerate the molecular sieve adsorbent to a residual water loading of a 2-5 wt %. There is no teaching or suggestion in Turnock et al of using a regeneration gas having a specified relative humidity for the purpose of substantially reducing the degradation/ageing of the adsorbent over repeated cycles.

In addition, there is absolutely no teaching or suggestion in Turnock et al of removing water from hydrocarbon gas stream using a zeolite having a pore diameter less than 5Å prior to contacting it with the molecular sieve having a pore diameter of at least 5Å to remove sulfur compounds. While Gingrich et al does disclose the use of a first adsorbent bed to remove water, Gingrich et al cannot logically be combined with Turnock et al, because the process in Gingrich et al involves removing sulfur-containing compounds from gases, i.e., it is a vapor-phase sweetening process. Turnock et al expressly states that: “it is well known that in vapor phase-sweetening processes, the presence of even relatively small amounts of water on the molecular sieve adsorbent has such an adverse effect on its selectivity and capacity as to render the operation commercially unfeasible” (col. 2, lines 10-14). (Underlining added for emphasis). Hence, one skilled in the art would not combine the liquid phase sulfur removal process of Turnock et al (which employs adsorbents having relatively high water loadings) with the gas phase sulfur removal process of Gingrich et al, because such combination according to Turnock et al would render the process unfeasible.

Conclusion

Claims 1, 5-7, 14, 16, 18 and 19 are patentable over GB ‘625 alone or in combination with Gingrich et al because neither of these references teach or suggest regenerating a sulfur loaded adsorbent by contacting the loaded adsorbent with a regeneration gas stream having the amounts of relative humidity specified in the claims. GB’ 625 uses a bleed stream of purified gas (gas from which water and sulfur compounds have been removed) for regeneration. There is absolutely no indication that the bleed stream of purified gas used for regeneration in GB ‘625 contains a relative water humidity, nor is there any teaching or suggestion in GB ‘625 that adding a small amount of water to the regeneration gas will significantly reduce degradation/ageing of a zeolite adsorbent over repeated cycles. Any water that appears in the regeneration off-gas in GB ‘625 is water that is removed from the adsorbent during regeneration of the adsorbent. It is not water that was ever present in, or added to, the regeneration gas to produce a relative water humidity.

Gingrich et al does not contain any teaching or suggestion relating to regeneration of loaded adsorbents and therefore adds nothing to GB ‘625 in this regard.

Accordingly, since neither GB ‘625 or Gingrich et al teach or reasonably suggest regenerating a sulfur loaded adsorbent by contacting the loaded adsorbent with a regeneration gas

stream having a specified relative humidity to reduce degradation/ageing, the rejection of claims 1, 5-7, 14, 16, 18 and 19 on the basis of these references is erroneous and should be reversed.

Claims 1, 7, 8, 10-12, 14, 16, 20, 21, and 23-25 are believed to be patentable over Sherman et al, Gingrich et al or Turnock et al, alone or in combination, because these references do not teach or reasonably suggest using a first zeolite having a pore diameter of less than 5Å, prior to contacting the hydrocarbon stream with a second zeolite adsorbent having a pore diameter of at least 5Å to adsorb the sulfur compounds, and regenerating a sulfur loaded adsorbent by contacting the loaded adsorbent with a regeneration gas stream having a specified relative humidity, which has been found to reduce degradation/ageing.

Sherman et al does teach the injection of water vapor into the hydrocarbon stream prior to a purge step. However, the purpose of the addition of water vapor is to import an adsorbed water loading of 0.7 to 3.0 wt % to the molecular sieve adsorbent, which percentage of water has been found to suppress COS formation. This is quite different from using a regeneration gas having a specified relative humidity for the purpose of substantially reducing the degradation/ageing of the adsorbent over repeated cycles.

Turnock et al discloses a process for removing sulfur compounds from liquid hydrocarbon streams using a zeolitic molecular sieve adsorbent having a relatively high water loading. The process includes a thermal-swing desorption step using a purge gas having a high water content, preferably steam, to regenerate the molecular sieve adsorbent to a residual water loading of a 2-5 wt %. There is no suggestion in Turnock et al of using a regeneration gas having a specified relative humidity for the purpose of substantially reducing the degradation/ageing of the adsorbent over repeated cycles.

Gingrich et al does not contain any teaching or suggestion relating to regeneration of loaded adsorbents, and therefore adds nothing to Sherman et al or Turnock et al in this regard. Gingrich et al does disclose water removal using a first zeolite bed, but is not properly combinable with Turnock et al, because Turnock et al teaches the presence of even small quantities of water on the molecular sieve adsorbent in a vapor-phase sweetening process of the type disclosed in Gingrich et al, “will render the operation commercially unfeasible“.

For all of the above reasons, it is believed that claims 1, 5-8, 10-12, 14, 16, 18-21 and 23-25 are patentable over the cited references. Accordingly, it is respectfully requested that the

action of the Examiner in finally rejecting these claims be reversed, and that the application be passed to issue.

Respectfully submitted,

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CLAIMS APPENDIX

The following claims are under appeal:

1. A process, comprising: removing water from a hydrocarbon stream, comprising water and sulfur compounds selected from the group consisting of hydrogen sulfide, carbonyl sulfides, mercaptans, especially C₁-C₆ mercaptans, organic sulfides, especially di-C₁-C₄-alkyl sulphides, organic sulfides, especially di-C₁-C₄-alkyl disulfides, thiophene compounds, aromatic mercaptans, especially phenyl mercaptan, and mixtures thereof, wherein the total amount of said sulfur compounds contained in the hydrocarbon stream is up to 3 vol%, based on total hydrocarbon stream, by adsorbing water therefrom onto a first zeolite having a pore diameter of less than 5 Å; and thereafter, contacting said hydrocarbon stream with an adsorbent comprising a second zeolite having a pore diameter of at least 5 Å to adsorb the sulfur compounds thereon to thereby provide a loaded adsorbent, followed by a regeneration of said loaded adsorbent in the presence of water by contacting said loaded adsorbent with a regeneration gas stream having a relative humidity of at most 30% and comprising an inert gas or an inert gas mixture.
5. A process according to claim 1, in which the hydrocarbon stream also comprises hydrogen sulfide and optionally carbon dioxide and up to 2 vol% hydrogen sulfide, with the hydrogen sulfide and part of the carbon dioxide being removed by means of washing the hydrocarbon stream with a chemical solvent.
6. A process according to claim 5, in which the temperature of the zeolite adsorption process is between 10 and 60 °C, the pressure is between 10 and 150 bara, and the superficial gas velocity is between 0.03 and 0.6 m/s.
7. A process for the regeneration of an adsorbent, wherein said process comprises: providing one or more vessels having a first adsorbent bed comprising a first zeolite having a pore diameter of 5 Å or less and a second adsorbent bed comprising a second zeolite having a pore diameter of more than 5 Å;

using said one or more vessels in the removal of sulfur from a hydrocarbon stream to provide said second zeolite that is loaded with sulfur; and
regenerating said second zeolite that is loaded with sulfur by contacting the adsorbent with a regeneration gas stream having a relative water humidity less than 100%.

8. A process according to claim 7, in which the adsorbent in said second adsorbent bed comprises zeolite dispersed in a binder.

10. A process according to claim 7, in which the regeneration is carried out at a pressure between 1 and 150 bara, a temperature between 200 and 400 °C, and a superficial gas velocity of less than 0.20 m/s.

11. A process according to claim 10, in which the regeneration gas stream is a gas stream obtained by saturating the stream at a temperature below the regeneration temperature.

12. A process according claim 11, in which the regeneration gas stream has a relative humidity between 0.1 and 30%.

14. A process for the removal of sulfur compounds from a hydrocarbon stream, wherein said hydrocarbon stream contains a sulfur compound selected from the group consisting of hydrogen sulfide, carbonyl sulfide, mercaptans, organic sulfides, organic disulfides, thiophene compounds, aromatic mercaptans and mixtures thereof, said process comprises:

treating said hydrocarbon stream to remove water therefrom followed by contacting said hydrocarbon stream with an adsorbent comprising a zeolite having a pore diameter of at least 5 Å to absorb said sulfur compound thereon to thereby provide a sulfur loaded adsorbent; and contacting said sulfur loaded adsorbent with a regeneration gas stream having a relative humidity of at most 30%, wherein the regeneration gas comprises an inert gas.

16. A process according to claim 14, wherein said mercaptans include C₁-C₆ mercaptans, said organic sulfides include di-C₁-C₄-alkyl sulfides, organic disulfides include di-C₁-C₄-alkyl

disulfides, said aromatic mercaptans include phenyl mercaptan, and the total amount of said sulfur compounds contained in said hydrocarbon stream is up to 3 vol% based on total gas stream.

18. A process according to claim 16, in which said hydrocarbon stream prior to contacting with said adsorbent, comprises hydrogen sulfide in the range up to 2 vol% hydrogen sulfide, and a part thereof is removed by means of washing with a chemical solvent.

19. A process according to claim 18, in which the temperature of the step of contacting said hydrocarbon stream with said adsorbent is between 10 and 60 °c, the pressure is between 10 and 150 bara, and the superficial gas velocity is between 0.03 and 0.6 m/s.

20. A process for the regeneration of an adsorbent, which is loaded with a sulfur compound, by contacting the adsorbent with a regeneration gas stream having a relative water humidity of at least 0.1% and less than 100%, wherein said adsorbent is contained in at least two beds, with one bed comprising a first zeolite having a pore diameter of up to 5 Å, and with a second bed comprising a second zeolite having a pore diameter of more than 5 Å.

21. A process according to claim 20, wherein said adsorbent of said second bed further comprises said second zeolite dispersed in a binder.

23. A process according to claim 21, in which the contacting step is carried out at a pressure between 1 and 150 bara, a temperature between 200 and 400 °C and a superficial gas velocity of less than 0.20 m/s.

24. A process according to claim 23, in which said regeneration gas stream is a gas stream obtained by saturating the stream at a temperature below the regeneration temperature.

25. A process according to claim 24, in which said regeneration gas stream has a relative humidity between 0.1 and 30%.

EVIDENCE APPENDIX

None

RELATED PROCEEDINGS APPENDIX

None